FE-NI-CO ALLOY THIN STRIP FOR SHADOW MASKS HAVING HIGH STRENGTH AND LOW COEFFICIENT OF THERMAL EXPANSION, ALONG WITH EXCELLENT MAGNETIC PROPERTIES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an Fe-Ni-Co alloy thin strip for shadow masks of press-formed type, particularly for ones for flat tubes. More particularly, the present invention relates to a Fe-Ni-Co alloy thin strip which is excellent in strength, coefficient of thermal expansion, etching properties and magnetic properties.

Description of the Related Art

In recent years, there have been increasing demands for a flat screen because of ease of watching images on such a screen, and materials of higher strength have been used for shadow masks so that even thin shadow masks have sufficient strength. For example, Japanese Patent Laid-Open No. 2001-262278 discloses a method of increasing strength of a material for shadow masks in which the material has a content of 27 to 47% Ni, 22% or less Co, 0.005 to 0.1% Nb, less than 0.01% C, 0.002 to 0.02% N, where $0.000013 \leq [\%Nb] \cdot [\%N] \leq 0.002$, a large number of fine-grained niobium nitride precipitates,

and fine grains with grain size of 10 or more in terms of the grain size number stipulated in JIS G 0551.

International Publication 01/59169A1 proposes a method of improving the yield strength and Young's modulus of a material for shadow masks in which the material has a content of 30 to 35% Ni, 2 to 8% Co, 0.01 to 0.5% Mn, and 0.01 to 0.8% the total of one or more of Nb, Ta and Hf.

An Fe-Ni-Co alloy, which has a low coefficient of thermal expansion compared with an Fe-36% Ni alloy and is expected to have a low thermal drift of electron beam, has begun to be used for shadow masks for flat tubes in which the incident angle of an electron beam becomes acute at the edge portion of a screen. And an Fe-Ni-Co alloy of which strength is increased by adding elements such as Nb has been used as a material for shadow masks for large-sized, 19 inches or more in size flat tubes. In larger-sized flat tubes, a phenomenon that an electron beam deviates from its normal orbit due to the external magnetic field becomes significant, in other words, the magnitude of the deviation, commonly referred to as magnetic drift, inevitably becomes large at the edge portion of a screen. The magnetic properties of an Fe-Ni-Co alloy are inferior to those of an Fe-36% Ni alloy. In addition, the elements, such as Nb, added to the alloy so as to increase its strength are likely to form carbides, nitrides and carbonitrides, and if a large number of those fine particles are precipitated as disclosed in Japanese Patent Laid-Open

No. 2001-262278 by, for example, performing an aging treatment at 800 to 900°C for several hours, the magnetic drift becomes very large.

The term "magnetic drift" herein used means a phenomenon that the orbit of an electron beam deviates from its normal orbit due to the magnetic field caused by the magnetization of a Braun tube or a cathod-ray tube, due to the earth (terrestrial) magnetism, which was once demagnetized in an alternating magnetic field. A shadow mask and an inner shield, which cover the front and the surroundings of a Braun tube or a cathod-ray tube, respectively, shield the Braun tube or the cathod-ray tube from the external magnetic field. Accordingly, when the magnetic properties of the material for a shadow mask were poor, magnetic shielding performance had to be ensured by increasing the thickness of the shadow mask or inner shield, in other words, incurring additional cost. Thus, there have been increasing demands for a shadow mask having excellent magnetic properties.

SUMMARY OF THE INVENTION

The present invention has been made in light of the above problem. Accordingly, the objective of the invention is to provide an Fe-Ni-Co alloy having both high strength and excellent magnetic properties, along with a low coefficient of thermal expansion.

The magnetic shielding performance of a shadow mask can be evaluated substitutionally by the coercive force as a direct current magnetic property of the shadow mask material which was subjected to heat treatment corresponding to an anneal before pressing. For example, when measuring the coercive force of a material, which was kept at 850°C for 15 minutes and cooled at a cooling rate of about 40°C/min, at the maximum magnetic field of 795 A/m (=10Oe), if the coercive force is 50 A/m or less, the material is taken as a material for a shadow mask which can be used for large-sized tubes 19 inches or more in size without causing any problems. Further, if the 0.2% yield strength of the material is 300 MPa or more after heat treatment, the material is taken as a material having sufficient resistance to external impact. And if the average coefficient of thermal expansion of the material from 25°C to 150°C is 1.2×10^{-6}/°C or less, the material is taken as a material having no problem of a thermal drift of electron beam.

In order to enhance satisfactorily these properties of the Fe-Ni-Co alloy containing Nb, the present inventors considered, as a method of improving the magnetic properties of the alloy without decreasing the strength, taking maximum advantage of elements in the solid solution state to improve the strength and magnetic properties thereof. As a result, the inventors have found that it is effective to decrease the amount of precipitates and to solid solution strengthen the

alloy by keeping the contents of the elements such as Nb, Mn, C, S and N, which are the sources of carbides, nitrides, sulfides and the compounds thereof, in suitable ranges and to produce crystal grains in a relatively large but proper size range, as measured before the alloy is pressed/annealed, and thus before it is etched through.

According to one aspect of the present invention, a phenomenon is utilized that growth of grain size and precipitation of carbides, nitrides, etc. are related to each other in the final stage of production of Fe-Ni-Co alloy of the present invention and a treatment for increasing grain size prevents precipitation of carbides, nitrides, etc., resulting in development of solid solution. Generally strength of alloys decreases when grain size is increased and precipitation is prevented; however, in the alloys of this invention, 0.2% yield strength of 300 MPa or more can be accomplished by reinforcing the solid solution. In the mean time, relatively large grain size allows the magnetic properties to be good.

According to another aspect of the present invention, attention is given to the amount of precipitates determined by the above-described phenomenon and the amount is considerably decreased. Although a decreased amount of precipitates results in decreased hardening, 0.2% yield strength of 300 MPa or more can be accomplished due to the reinforcement of the solid solution by Nb. The solid solution

Nb does not directly improve the magnetic properties by itself, but a small amount of precipitates and a decreased amount of inclusions indirectly contribute to good magnetic properties.

The present inventors have also found that in the Fe-Ni-Co alloy system, the coercive force can be reduced directly by bringing Si to the solid solution state.

The present invention is:

(1) an Fe-Ni-Co alloy thin strip for shadow masks having high strength and a low coefficient of thermal expansion, along with excellent magnetic properties, including, on a mass basis, 30 to 35% Ni, 2 to 6% Co, 0.1 to 0.4% Nb, 0.2 to 0.5% Mn, and the rest Fe and unavoidable impurities, wherein the unavoidable impurities includes 0.005% or less C, 0.002% or less S and 0.005% or less N and the grain size before etching through the strip is 7.0 to 10.0 in terms of grain size number stipulated in JIS G 0551,

(2) an Fe-Ni-Co alloy thin strip for shadow masks having high strength and a low coefficient of thermal expansion, along with excellent magnetic properties, including, on a mass basis, 30 to 35% Ni, 2 to 6% Co, 0.1 to 0.4% Nb, 0.2 to 0.5% Mn, and the rest Fe and unavoidable impurities, wherein the unavoidable impurities includes 0.005% or less C, 0.002% or less S and 0.005% or less N and precipitates and inclusions are 0.2 μm to 5 μm in size and the total mass of them is 0.5 μg/mm³ to 1.5 μg/mm³, and

(3) the Fe-Ni-Co alloy thin strip for shadow masks having high strength and a low coefficient of thermal expansion, along with excellent magnetic properties according to (1) or (2), further including 0.03 to 0.10% Si in the solid solution state.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following the embodiment of this invention will be described in detail.

The feature of the Fe-Ni-Co alloy of this invention is that maximum advantage of the solid solution of the elements in the alloy, such as Nb, is taken in its strength and magnetic properties. In the Fe-Ni-Co alloy of this invention, a good balance of strength and magnetic properties is accomplished by allowing the content of Nb to be in the solid solution range suitable for increasing the strength and decreasing the amount of impurities which are the sources of precipitates. In addition to the composition adjustment, preferably precipitates are resolved by heat treatment to decrease their amount.

Further, in the Fe-Ni-Co alloy of this invention, the good balance of strength and magnetic properties after final rolling is accomplished also by allowing its grain size to be in the suitable range.

Preferably, Si is allowed to exist in the alloy not as precipitates or inclusions, but as solutes.

The amount of solid solution Si is determined by SIMS (secondary ion mass spectrometry), specifically the value is taken as the amount of Si in the solid state which is quantitatively determined by scanning the surface of a test piece of the alloy 100 μm square at the position where no intensively localized Si is detected (no precipitates and no inclusions) and when is observed no large change in concentration profile of Si during the analysis.

The amount of precipitates and inclusions is quantitatively evaluated by the following method.

First the alloy thin strip is immersed in 10 v/v% acetylacetone - 1 v/v% tetramethylammonium chlorides - methyl alcohol electrolysis solution and 10 g of the alloy is dissolved by controlled current electrolysis at a current density of 400 A/m^2 or less (two-electrode type, quantity of electricity of 3360 coulomb/g).

The solution where 10 g of the alloy was dissolved is filtered through a membrane filter having pores 5 μm in diameter, the obtained filtrate is further filtered through a filter having pores 0.2 μm in diameter, and the increase in mass of the 0.2 μm-pore filter after drying is taken as the amount of inclusions and precipitates 0.2 μm to 5 μm in size.

The amount of inclusions and precipitates 0.2 μm to 5 μm in size per unit volume is obtained by dividing the increased mass by the volume of the dissolved alloy strip.

The precipitates and inclusions as the filtration residue in the above method are fine particles of NbN, NbC, MnS, Al_2O_3, SiO_2, MnO, MgO and the composite thereof and the aggregates of the above fine particles in the form of clusters. Although the aggregates are different in shape and they take shape of, for example, a sphere, ellipse, rod, etc., the size of the precipitates and inclusions in the present invention is determined by whether or not they are filtered or not through membrane filters of predetermined mesh sizes after electrolysis in accordance with the above method.

In the following the reasons will be described why the composition etc. of the present invention are limited.

Nb: If the content of Nb is too small, the strength of the alloy strip cannot be sufficiently improved without the use of precipitates or the magnetic properties deteriorate, with the use of precipitates whereas if the content of Nb is too large, the coefficient of thermal expansion of the alloy becomes large. Thus, the content of Nb in the alloy is within the limit of 0.1 to 0.4%.

Mn: If the content of Mn is too small, segregation of nickel sulfide occurs at the grain boundaries and thereby the deterioration of hot-workability is unavoidable, whereas if the content of Mn is too large, the coefficient of thermal expansion becomes large and a large amount of MnS causes the deterioration of magnetic properties. Thus, the content of Mn in the alloy is within the limit of 0.2 to 0.5%.

C: If the content of C is too large, the amount of carbide and carbonitride increases, resulting in deterioration of the magnetic properties. Thus, the content of C in the alloy is within the limit of 0.005% or less.

S: If the content of S is too large, hot cracking is likely to occur in the alloy and a large amount of MnS causes the deterioration of the magnetic properties. Thus, the content of S in the alloy is within the limit of 0.0020% or less, preferably less than 0.0010%.

N: If the content of N is too large, the amount of nitride and carbonitride increases, resulting in deterioration of the magnetic properties. Thus, the content of N in the alloy is within the limit of 0.005% or less.

Si: Si exists in the alloy as solid solution Si, and the larger the amount of solid solution Si, the better the magnetic properties of the alloy. The effect is not sufficient if the content of solid solution Si is less than 0.03%. However, if the content of solid solution Si is more than 0.10%, the coefficient of thermal expansion of the alloy increases, moreover, a large amount of smut is produced when etching the alloy, whereby the etching nozzles are likely to clog. Thus, the content of solid solution Si in the alloy is within the limit of 0.03% to 0.10%.

Grain size: If the grain size of number stipulated in JIS G 0551 the alloy before etching through the alloy strip is smaller than 7.0, the grain size is too large, whereby holes

with rough edge are produced by etching. In addition, the strength as a shadow mask is not enough to be resistant to external impact. If the grain size number is larger than 10.0, the grain size is too small, whereby even if the amount of precipitates is decreased, sufficient magnetic shielding performance cannot be obtained. Thus the suitable range of the grain size is 7.0 to 10.0 in terms of the grain size number stipulated in JIS G 0551.

Precipitates and Inclusions: There exist in the Fe-Ni-Co alloy of the present invention Al_2O_3, SiO_2, MgO, MnO, and the compounds and composites thereof, which are produced when the alloy is melted, and are changed in shape by plastic deformation but hardly changed in amount in the processes after the melting. They also exist NbC, NbN, the compounds thereof, and MnS, which form when the alloy is solidified, and may change in amount by heating in hot working process and annealing between cold rolling processes. The size of the precipitates and inclusions that prevents the movement of the magnetic domain wall and affects the magnetic properties is relatively small, and when the size is longer than 5 μm, the effects are negligible. On the other hand, it is difficult to accurately detect the precipitates and inclusions smaller than 0.2 μm in size. After experiments, the present inventors found that the good or bad of the magnetic properties can be judged from the amount of the precipitates and inclusions 0.2 μm to 5 μm in size. The

smaller the amount of precipitates and inclusions having the size in such a range becomes, the better the magnetic properties become. However, with the decrease in such an amount, the strength of the alloy is also decreases; thus, in order to make a good balance of the magnetic properties and the strength, the amount of the precipitates and inclusions is preferably within the limit of 0.5 $\mu g/mm^3$ to 1.5 $\mu g/mm^3$, more preferably 0.5 $\mu g/mm^3$ to 1.0 $\mu g/mm^3$.

Examples

In the following the present invention will be described in terms of its Examples.

Specified materials were melted by VIM method to give the composition shown in Table 1 and cast to approximately 500 kg ingots. Then the ingots were heated in the temperature range of 1250°C to 1300°C for 5 hours or longer and forged into slabs about 100 mm thick. After scalped, the slabs were heated and hot rolled at 1150°C to 1250°C to give hot rolled sheets about 3 mm thick. After descaling the hot rolled sheets by pickling, the sheets were cold rolled and annealed repeatedly to give thin strips 0.15 mm thick. The grain size and the amount of the precipitates were changed by changing the ultimate temperature of the materials in the annealing (final annealing) just before the cold rolling (final rolling) for producing thin strips 0.15 mm thick, within the range of 800°C to 1100°C and controling the time during which the materials were kept at about 700°C or higher, higher than

the recrystallization temperature, within the range of 5 to 60 seconds. Specifically, if the ultimate temperature of the materials is low and the time during which the materials are kept at temperatures higher than the recrystallization temperature is short, the grain size decreases, the amount of the precipitations increases, and the amount of solid solution decreases. The alloys of Embodiments No. 1 to No. 8 of the present invention were prepared by setting the materials' ultimate temperature for 1000°C to 1100°C and the time during which the materials were kept higher than the recrystallization temperature for 15 to 40 seconds. Although the rolling reduction ratio of the final cold rolling was set for 25%, the rolling reduction ratio is not limited to this as long as it is in the range of 15% to 45%.

Table 1

Composition No.	C	Mn	S	Ni	Co	Nb	N
A	0.002	0.22	0.0008	32.1	5.0	0.32	0.0028
B	0.004	0.25	0.0012	32.0	4.9	0.11	0.0022
C	0.001	0.32	0.0015	32.5	5.0	0.25	0.0022
D	0.004	0.37	0.0006	31.8	4.0	0.22	0.0024
E	0.003	0.32	0.0010	33.5	3.4	0.28	0.0023
F	0.004	0.27	0.0007	32.1	5.0	0.25	0.0036
G	0.003	0.27	0.0005	32.0	4.9	0.25	0.0032
H	0.004	0.25	0.0012	32.0	4.9	0.11	0.0022
I	0.008	0.26	0.0012	32.8	4.2	0.15	0.0042
J	0.004	0.15	0.0018	32.1	5.4	0.25	0.0028
K	0.003	0.55	0.0015	32.2	5.1	0.30	0.0032
L	0.003	0.28	0.0026	32.0	4.3	0.31	0.0035
M	0.003	0.25	0.0015	36.1	1.5	0.30	0.0032
N	0.004	0.02	0.0013	32.1	9.5	0.06	0.0028
O	0.003	0.25	0.0015	32.4	5.1	0.45	0.0034
P	0.003	0.26	0.0013	29.3	5.2	0.10	0.0067
Q	0.003	0.27	0.0017	32.0	5.1	0.01	0.0032

The amount of solid solution Si, grain size number (GS. No.), amount of precipitates, and etchability were examined for the produced materials for shadow mask. And after the materials were kept in 8% H_2-N_2 atmosphere at 850°C for 15 minutes and cooled at a rate of about 40°C/min, the coercive force, 0.2% yield strength, coefficient of thermal expansion (average coefficient of thermal expansion from 25°C to 150°C) of the materials were evaluated.

The etching properties was examined in the steps of: applying well-known photolithography to the alloy strips produced through the above process to form resist masks having a large number of circular apertures 80 μm in diameter on one face of the thin strip (cut into a 50 mm square) and circular apertures 180 μm in diameter on the other face at the opposite position; spraying ferric chloride aqueous solution of 45 Baumé on the resist masks at 50°C to form through-holes; and observing the shape of the etched through-holes, while observing the amount of smut produced through filtering the ferric chloride aqueous solution after etching.

The measured results are shown in Table 2.

Table 2

No.	Composition No.	Solid Solution Si (%)	Grain Size No.	Amount of Precipitates and Inclusions ($\mu g/mm^3$)	Coercive Force (A/m)	0.2% Yield Strength (MPa)	Coefficient of Thermal Expansion ($10^{-6}/°C$)	Etching Properties	
1	A	0.05	8.3	1.2	41	326	1.0	no problem	Inventive Examples
2	B	0.04	9.6	1.3	44	332	0.9	no problem	
3	C	0.05	8.5	0.9	38	322	1.0	no problem	
4	D	0.07	8.0	1.0	39	324	1.0	no problem	
5	E	0.05	7.6	1.1	38	318	1.1	no problem	
6	F	0.02	7.9	1.1	48	328	1.0	no problem	
7	G	0.12	7.7	1.2	40	338	1.2	a large amount of smut	
8	H	0.04	9.6	0.7	35	317	0.9	no problem	
9	A	0.05	10.3	1.2	58	338	1.2	no problem	Comparative Examples
10	B	0.05	6.6	1.1	32	287	1.0	holes with rough edge	
11	I	0.05	8.1	1.7	55	327	1.2	no problem	
12	J	0.05	8.6	1.3	52	325	0.9	no problem	
13	K	0.05	8.6	1.6	49	322	1.7	no problem	
14	L	0.05	8.0	1.8	58	331	1.1	no problem	
15	M	0.05	8.0	1.5	46	290	2.2	no problem	
16	N	0.05	8.0	0.6	29	302	1.9	no problem	
17	O	0.05	9.7	1.9	62	338	1.4	no problem	
18	P	0.05	8.3	1.2	69	342	1.6	no problem	
19	Q	0.04	7.9	0.7	28	280	1.1	no problem	

All the thin strips produced in the Embodiments of this invention showed good coercive force, coefficient of thermal expansion and etching properties. Of the thin strips of this invention, those of Embodiments No. 6 (alloy F) and No. 7 (alloy G) contained solid solution Si in amount outside the range claimed in claim 4. Since the thin strip of Embodiment No. 6 contained a smaller amount of solid solution Si than those of the other Embodiments of this invention, its coercive force was not very good, whereas since the thin strip of Embodiments No. 7 contained a larger amount of solid solution Si, its coefficient of thermal expansion was large and the amount of smut produced during etching was also large.

The thin strips of Comparative Examples No. 9 (alloy A) and No. 10 (alloy B) had grain size outside the range claimed in claims 1 and 3. Since the grain size number of the thin strip of Comparative Example No. 9 was too large, its coercive force was not very good, whereas since the grain size number of the thin strip of Comparative Example No. 10 too small, its 0.2% yield strength was not sufficient in terms of resistance to impact and the holes produced by etching had rough edge. In the thin strips of Comparative Examples No. 11 (alloy I) and No. 19 (alloy Q), any one or more of the contents of their composition were outside the range claimed in claims 1 and 2. The coercive force of the thin strips of Comparative Examples No. 11 and 12 were large since the thin strip of Comparative Example No. 11 had too large C content

and that of Comparative Example No. 12 too small Mn content. The reason why the thin strip of Comparative Example No. 12 had a large coercive force is possibly that the amount of solid solution Mn was too small. The thin strip of Comparative Example No. 13 had a large coefficient of thermal expansion, since it had too much Mn, and it was not at sufficient level in terms of thermal drift of electron beam. The thin strip of Comparative Example No. 14 had a large amount of precipitates and a large coercive force, since it contained too much S. The thin strips of Comparative Examples No. 15, 16 and 18 had a large coefficient of thermal expansion and were not at sufficient level in terms of thermal drift of electron beam, since those of Comparative Examples No. 15, No. 16 and No. 18 had both Ni and Co contents, only Co content, and only Ni content outside the range claimed in claims 1 and 2, respectively. The thin strip of Comparative Example No. 18 had a large amount of precipitates and a large coercive force, since it contained too much N. The thin strip of Comparative Example No. 17 had a large amount of precipitates, a large coercive force and a large coefficient of thermal expansion, since the Nb content was too large. In the thin strip of Comparative Example No. 19, its 0.2% yield strength was not at sufficient level in terms of resistance to impact, since it had too small Nb content.

As described above, the thin strips of Comparative Examples No. 9 to No. 19 had problems of some kind as materials

used for a shadow mask for flat tubes, particularly for a shadow mask for large-sized flat tubes 19 inches or larger in size.

According to the present invention, an Fe-Ni-Co alloy thin strip for shadow masks which is highly resistant to external impact and excellent in magnetic shielding performance can be provided. The use of this alloy thin strip allows shadow masks, particularly shadow mask of a type which is used for large-sized flat tubes or Braun tubes or cathod-ray tubes to which a speaker is adjacent, to be thin compared with those commonly used, and in addition, allows the production of Braun tubes or cathod-ray tubes at low cost, because additional cost need not be incurred for inner shield materials and correction circuits.